J|A|C|S COMMUNICATIONS

Synthesis of a Nitrido-Substituted Analogue of the Uranyl Ion, $[N{=}U{=}O]^+$

Skye Fortier, Guang Wu, and Trevor W. Hayton*

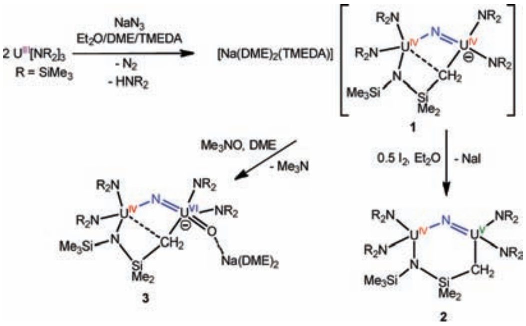
Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106

Received February 23, 2010; E-mail: hayton@chem.ucsb.edu

Uranyl (UO_2^{2+}) is a robust chemical species that contains strong U≡O triple bonds and oxo ligands that are resistant to chemical elaboration.[1,2] However, the recent isolation of its *bis*(imido) analogue, $[U(NR)_2]^{2+}$,[2,3] suggests that substitution of the O^{2-} ligands in UO_2^{2+} with other isolobal fragments may be possible, provided a viable synthetic pathway can be discovered. In particular, given the frontier orbital similarity between O^{2-} and N^{3-}, the nitrido-substituted analogues of uranyl, namely $[NUO]^+$ and [NUN], appear to be reasonable synthetic targets.[4−6] These materials would offer an excellent opportunity to study actinide-ligand multiple bonding and uncover potentially novel N-atom transfer reactivity.[2] However, actinide nitrido complexes remain scarce, and only a few molecular uranium nitrides have been characterized.[7−12]

We recently reported the synthesis of a series of uranium azides, including $\{[Na(THF)_4][U[NR_2]_3(N_3)_2]\}_x$ (R = $SiMe_3$).[13] However, attempts to induce nitride formation from these U^{4+} materials have failed, prompting us to investigate synthetic routes involving U^{3+}, a significantly stronger reductant[14] and known precursor to molecular uranium nitrides.[7−9,11,12] Thus, addition of 0.5 equiv of NaN_3 to a dark purple solution of $U(NR_2)_3$ results in gas evolution and formation of a red-orange solution from which the U(IV) bridged-nitrido complex $[Na(DME)_2(TMEDA)][(NR_2)_2U(\mu\text{-}N)(\mathit{C}H_2SiMe_2\mathit{N}R)U(NR_2)_2]$ (**1**) can be isolated in 69% yield (Scheme 1).

Scheme 1



The formation of **1** arises from the two-electron reduction of azide by two molecules of $U(NR_2)_3$, to generate a nitrido ligand bridged by two U(IV) centers. Surprisingly, nitride formation is accompanied by the deprotonation of a methyl group by $[NR_2]^-$, yielding a μ-CH_2 moiety and HNR_2. The presence of the latter in the reaction mixture was confirmed by ^1H NMR spectroscopy. The deprotonation of $SiMe_3$ groups has been observed previously in transition metal,[15] lanthanide,[16] and actinide systems.[17−19]

The solid-state molecular structure of **1** exhibits U—$N_{nitride}$ bond distances of U1—N1 = 1.95(1) Å and U2—N1 = 2.12(1) Å (Figure 1). These inequivalent U—$N_{nitride}$ bond lengths are suggestive of localized U—N═U bonding interactions,[7,20,21] differing from the equivalent U═N═U bonds observed in $[(C_5Me_5)_2U(\mu\text{-}N)U(\mu\text{-}N_3)(C_5Me_5)_2]_4$.[7] This asymmetry may be due to the acute U1—N1—U2 bond angle (123.5(5)°), likely caused by the bridging nature of the methylene group. The μ-CH_2 interactions in **1** are also inequivalent, as the U1—C1 distance (2.51(1) Å) is considerably shorter than the U2—C1 distance (2.88(1) Å).

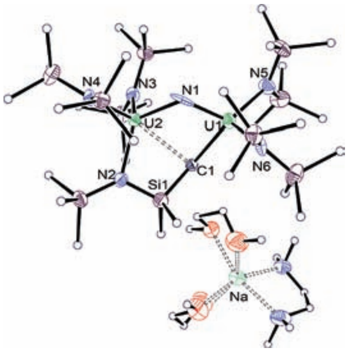


Figure 1. Solid-state molecular structure of $[Na(DME)_2(TMEDA)][(NR_2)_2U(\mu\text{-}N)(\mathit{C}H_2SiMe_2\mathit{N}R)U(NR_2)_2]$ (**1**) with 50% probability ellipsoids.

Given the unique U—N═U bridging interactions in **1**, we investigated the effect of oxidation upon the U—$N_{nitride}$ bond lengths. Complex **1** is readily oxidized by 0.5 equiv of I_2, affording the formally mixed-valent U(IV/V) complex $(NR_2)_2U(\mu\text{-}N)(\mathit{C}H_2SiMe_2\mathit{N}R)U(NR_2)_2$ (**2**) in 57% yield (Scheme 1). The solid-state molecular structure of **2** (see the Supporting Information) reveals U—$N_{nitride}$ bond lengths of U1—N1 = 1.909(6) Å and U2—N1 = 2.201(6) Å. The former is comparable to the U—$N_{nitride}$ distance found in the U(V) nitridoborate $[N^nBu_4][(C_6F_5)_3B{-}N{\equiv}U(N[^tBu]Ar)_3]$ (1.916(4) Å) (Ar = 3,5-$Me_2C_6H_3$).[9] More importantly, the difference between the U1—N1 and U1—N2 bond lengths in **2** (0.29 Å) is larger than the difference observed in **1** and is strongly suggestive of localized U(IV) and U(V) valence states. Additionally, the methylene carbon is no longer bridging and only one U—C (U1—C1 = 2.427(8) Å) interaction is retained.

Oxidation of **2** with either I_2 or AgOTf fails to produce a U(V/V) complex and only results in formation of intractable mixtures. However, oxidation of **1** with 1 equiv of trimethylamine *N*-oxide (Me_3NO) rapidly generates $[Na(DME)_2][(NR_2)_2(O)U(\mu\text{-}N)(\mathit{C}H_2SiMe_2\mathit{N}R)U(NR_2)_2]$ (**3**) in 84% yield (Scheme 1) via oxygen atom transfer. A similar O-atom transfer was used to generate $Cp^*_2U(NAr)(O)$ from $Cp^*_2U(NAr)$ (Ar = 2,6-$^iPr_2C_6H_3$).[22]

Complex **3** contains a sodium-capped oxo ligand which is coordinated *trans* to the nitrido ligand (O1—U1—N1 = 167.6(3)°), creating a geometry that is reminiscent of the uranyl ion (Figure 2).[1] The metrical parameters of this unprecedented $[OUN]^+$ fragment are marked by short U—$N_{nitride}$ (U1—N1 = 1.818(9) Å) and U—O_{oxide} (U1—O1 = 1.797(7) Å) bond lengths, strikingly similar to the metrical parameters of both UO_2^{2+} and its oxo-imido analogue $[U(N^tBu)O]^{2+}$.[23] For further comparison, the U—$N_{nitride}$ distance in the U(VI) nitride, $(C_6F_5)_3B{-}N{\equiv}U(N[^tBu]Ar)_3$, is 1.880(4) Å.[9] Interestingly, the U2—N1 interaction (2.284(8) Å) lengthens upon formation of $[OUN]^+$, relative to that observed for **2**. This lengthening is further exemplified by the

10.1021/ja101567h

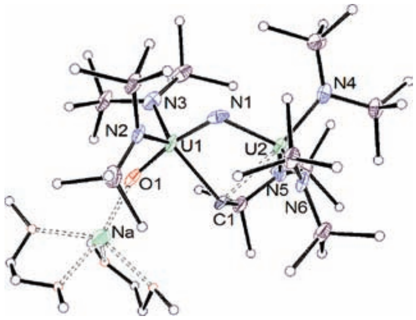


Figure 2. Solid-state molecular structure of $[Na(DME)_2][(NR_2)_2(O)U(\mu\text{-}N)(\mathit{C}H_2SiMe_2\mathit{N}R)U(NR_2)_2]\cdot{}^1/_4Et_2O\cdot{}^3/_4C_5H_{12}$ ($\mathbf{3}\cdot{}^1/_4Et_2O\cdot{}^3/_4C_5H_{12}$) with 50% probability ellipsoids.

bond length disparity between U1−N1 and U2−N1 (0.47 Å), which is significantly greater than that found for either **1** (0.17 Å) or **2** (0.29 Å).

Complex **3** can be formally described as either a U(V/V) or a U(VI/IV) dimer. We prefer the latter description, in part because the metrical parameters of the uranyl-like $[OUN]^+$ fragment support the presence of a U^{6+} ion in the oxo-ligated uranium center. Additionally, μ_{eff} for **3** is 3.34 μ_B at 290 K, which is consistent with the presence of a single U^{4+} ion.[24] This value is close to the theoretical value of 3.58 μ_B calculated for a free $5f^2$ ion.[24] It should be noted, however, that the temperature dependence of μ_{eff} is at odds with that typically seen for a $5f^2$ ion[25] but is similar to that recently reported for $Li[U(CH_2R)_5]$ (R = $SiMe_3$, ^{t}Bu).[26]

The magnetic properties of **1** and **2** have also been assessed by SQUID magnetometry, as the bridging nitride interactions offer the possibility of observing magnetic communication between actinide centers.[27] The effective magnetic moments for **1** and **2** at 290 K are 4.14 μ_B and 3.48 μ_B per molecule, respectively (Figure 3). These values are less than those anticipated for the sum of the free ions. For instance, the 2.07 μ_B per U^{4+} ion in **1** is significantly smaller than the theoretical free ion value.[24] Other uranium amides display similar μ_{eff} values,[28,29] an observation that has been ascribed to the quenching of spin−orbit coupling arising from covalent metal−ligand interactions.[24]

The χ versus T plots for either **1** or **2** (see the Supporting Information) do not reveal a maxima indicative of antiferromagnetic coupling between uranium centers. The lack of obvious magnetic communication within these complexes may be due to the localized bonding interactions of the bridging nitrido ligand (as suggested by the inequivalent $U-N_{nitride}$ distances). The magnetization data, however, does show a clear decrease in μ_{eff} from **1** to **3**, consistent with the reduction of spin multiplicity upon oxidation.

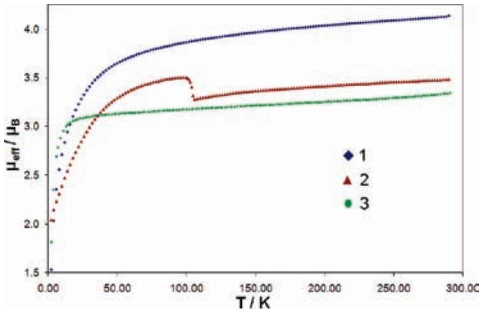


Figure 3. Temperature-dependent SQUID magnetization data for **1**−**3**.

Interestingly, a plot of μ_{eff} versus T for **2** (Figure 3) exhibits a sudden increase in μ_{eff} on cooling below 105 K. This transition is field independent and retraceable upon warming from 2 K. Similar phenomena in other f-element complexes have been rationalized by the presence of a crystallographic phase transition.[30] Measurement of the unit cell parameters for a single crystal of **2** from 150 to 80 K indeed reveals a semireversible phase transition, from the monoclinic crystal system to the triclinic system, on cooling below 90 K.

In summary, we have synthesized a uranium complex containing the unprecedented oxo-nitrido $[OUN]^+$ fragment, further clarifying the idea that uranium ligand multiple bonding is strengthened within a uranyl-like fragment. We will continue to examine the reactivity and magnetic properties of these complexes and also attempt to develop synthetic routes to the as yet unknown UN_2 fragment.

Acknowledgment. Financial support was provided by UCSB. S.F. was supported in part by a Graduate Opportunity Fellowship from UCSB. We thank Brent C. Melot for assistance with the SQUID measurements.

Supporting Information Available: Experimental procedures, crystallographic details (as CIF files), magnetic susceptibility plots, and spectral data for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Denning, R. G. *J. Phys. Chem. A* **2007**, *111*, 4125–4143.
(2) Hayton, T. W. *Dalton Trans.* **2010**, *39*, 1145–1158.
(3) Hayton, T. W.; Boncella, J. M.; Palmer, P. D.; Scott, B. L.; Batista, E. R.; Hay, P. J. *Science* **2005**, *310*, 1941–1943.
(4) Kaltsoyannis, N. *Inorg. Chem.* **2000**, *39*, 6009–6017.
(5) Hunt, R. D.; Yustein, J. T.; Andrews, L. *J. Chem. Phys.* **1993**, *98*, 6070.
(6) Zhou, M. F.; Andrews, L. *J. Chem. Phys.* **1999**, *111*, 11044–11049.
(7) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Science* **2005**, *305*, 1835.
(8) Evans, W. J.; Miller, K. A.; Ziller, J. W.; Greaves, J. *Inorg. Chem.* **2007**, *46*, 8008–8018.
(9) Fox, A. R.; Cummins, C. C. *J. Am. Chem. Soc.* **2009**, *131*, 5716–5717.
(10) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 3433–3436.
(11) Nocton, G.; Pécaut, J.; Mazzanti, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3040–3042.
(12) Fox, A. R.; Cummins, C. C. *J. Am. Chem. Soc.* **2010**, *132*, 3250–3251.
(13) Fortier, S.; Wu, G.; Hayton, T. W. *Dalton Trans.* **2010**, *39*, 352–354.
(14) Evans, W. J.; Kozimor, S. A. *Coord. Chem. Rev.* **2006**, *250*, 911–935.
(15) Yu, X.; Bi, S.; Guzei, I. A.; Lin, Z.; Xue, Z.-L. *Inorg. Chem.* **2004**, *43*, 7111–7119.
(16) Marc, K.; Klaus, H.; Gerd, S.; Werner, M.; Stefan, F.; Gernot, F.; Kurt, D. *Z. Anorg. Allg. Chem.* **1999**, *625*, 2055–2063.
(17) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7728–7729.
(18) Graves, C. R.; Schelter, E. J.; Cantat, T.; Scott, B. L.; Kiplinger, J. L. *Organometallics* **2008**, *27*, 5371–5378.
(19) Gardner, B. M.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *J. Am. Chem. Soc.* **2009**, *131*, 10388–10389.
(20) Wheeler, R. A.; Hoffmann, R.; Straehle, J. *J. Am. Chem. Soc.* **1986**, *108*, 5381–5387.
(21) Wheeler, R. A.; Whangbo, M. H.; Hughbanks, T.; Hoffmann, R.; Burdett, J. K.; Albright, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 2222–2236.
(22) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448–9460.
(23) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Batista, E. R. *J. Am. Chem. Soc.* **2006**, *128*, 12622–12623.
(24) Castro-Rodriguez, I.; Olsen, K.; Gantzel, P.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 4565–4571.
(25) Castro-Rodríguez, I.; Meyer, K. *Chem. Commun.* **2006**, 1353–1368.
(26) Fortier, S.; Melot, B. C.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2009**, *131*, 15512–15521.
(27) Spencer, L. P.; Schelter, E. J.; Yang, P.; Gdula, R. L.; Scott, B. L.; Thompson, J. D.; Kiplinger, J. L.; Batista, E. R.; Boncella, J. M. *Angew. Chem., Int. Ed.* **2009**, *121*, 3853–3856.
(28) Reynolds, J. G.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 2822–2825.
(29) Reynolds, J. G.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M.; Templeton, L. K. *Inorg. Chem.* **1976**, *15*, 2498–2502.
(30) Walter, M. D.; Berg, D. J.; Andersen, R. A. *Organometallics* **2006**, *25*, 3228–3237.

JA101567H